

FUNDAMENTAL MECHANISMS OF ELECTRODE KINETICS AND ALKALI METAL ATOM TRANSPORT AT THE ALKALI β -ALUMINA / POROUS ELECTRODE / ALKALI METAL VAPOR THREE PHASE BOUNDARY

R. M. Williams, B. Jeffries-Nakamura, M. A. Ryan, M. L. Underwood, D. O'Connor, A. Kisor, and S. K. Kikkert

The mechanisms of electrode kinetics and mass transport of alkali metal oxidation and alkali metal cation transport at the solid electrolyte porous electrode boundary as well as alkali metal transport through porous metal electrodes has important applications in optimizing device performance in alkali metal thermal-to-electric converter (AMTEC) cells which are high temperature, high current density electrochemical cells. Basic studies of these processes also affords the opportunity to investigate a very basic electrochemical reaction over a wide range of conditions; and a variety of mass transport modes at high temperatures via electrochemical techniques. The temperature range of these investigations covers 700K to 1240K; the alkali metal vapor pressures range from about 10^{-2} to 10^2 Pa; and electrodes studied have included Mo, W, $\text{Mo}/\text{Na}_2\text{MoO}_4$, $\text{W}/\text{Na}_2\text{WO}_4$, WPt_x , and WRh_x ($1.0 < x < 6.0$) with Na at Na- β -alumina, and Mo with K at K- β -alumina. Both liquid metal/solid electrolyte/ alkali metal vapor and alkali metal vapor/solid electrolyte/ vapor cells have been used to characterize the reaction and transport processes.

Experimental and modeling studies of the exchange current at the alkali (Na,K) β -alumina/ porous electrode/ alkali metal vapor three phase boundary have indicated that the microscopic mechanism of the alkali ion - electron recombination reaction can be accounted for by a electron tunneling and the collision frequency of the reactants. The three phase boundary zone is formed by a porous refractory metal electrode with a contact zone about 10^4 - 10^5 cm long per cm^2 of geometric surface area. The rate of reaction of alkali metal vapor on the surface of an alkali β -alumina solid electrolyte (BASE) ceramic has been studied by comparison of the expected rates for the three simplest reaction mechanisms with known temperature dependent rate data; and the physical parameters of typical porous metal electrode/BASE/alkali metal vapor reaction zones. The three simplest reactions are tunneling of electrons from the alkali coated electrode to a surface bound alkali metal ion; emission of an electron from the electrode with subsequent capture by a surface bound alkali metal ion; and thermal emission of an alkali cation from the BASE and its capture on the porous metal electrode surface where it may recombine with an electron. Only the first reaction adequately accounts for both the high observed rate and its temperature dependence, and agree with observed rates of reaction within the accuracy permitted by uncertainty in morphological parameters of the interphase zone.

We have previously reported evidence of ionic, free molecular flow, and surface transport of sodium in several types of AMTEC electrodes. Quantitative investigations of Na transport through $\text{WPt}_{3.5}$ via surface or grain boundary diffusion, and K transport through porous Mo electrodes by free molecular flow, over large ranges of temperature have been performed. $\text{WPt}_{3.5}$ has especially low transport impedance over the 950 to 1200K temperature range. New results on the transport and electrode kinetics of Na at porous $\text{WPt}_{3.5}$ from 830K to 1210K are reported.